Synthetic 'deweylite'

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SUMMARY. Materials similar to the natural hydrated magnesium silicate mineral deweylite have been synthesized hydrothermally under low-temperature–low-pressure conditions from magnesia–silica gels. Optical, X-ray, infra-red, and DTA examinations have shown that both the natural and synthetic materials are mixtures of badly crystallized talc and badly crystallized serpentine. The mineral is thought to be a coarse mixture of these two components while the synthetic products are intimately interlayered. These materials are believed to be closely related to the hydrated magnesium silicates detected in high-magnesia cement hydration products.

AN investigation into the nature of the magnesia-bearing phases formed during the hydration of high-magnesia cements has led to an examination of the mineral 'deweylite'.

High levels of MgO in Portland cements result from the use of dolomitic limestones in countries where high-grade limestones are either not available or are in short supply. Provided the amount of magnesia is less than 5 % the cement behaves normally, but expansion and cracking can result when amounts greater than this are present. The volume increase consequent on the hydration of periclase to brucite is believed to be chiefly responsible for this phenomenon. Cements containing up to 15 % MgO can be stabilized against expansion, both during room-temperature curing and under hydrothermal conditions, by adding reactive silicate materials such as trass, fly-ash, slag, etc. (Rosa, 1965; Majumdar and Rehsi, 1969). Although the mechanism responsible for the stabilization is still open to question it has been suggested (Majumdar and Rehsi, 1969) that the formation of a poorly crystallized magnesium silicate hydrate may play some part in the process. Similarities between the X-ray powder patterns of 'deweylite' and a component of high-magnesia cements stabilized with fly-ash caused the authors to examine the mineral and attempt its synthesis.

There appears to be considerable confusion over the naming of the group of poorly crystallized magnesium silicate hydrate and nickel magnesium silicate hydrate minerals. Over the years there has been a proliferation of names including garnierite, gymnite, genthite, deweylite, nepouite, noumeïte, etc., several of which refer to materials that are essentially identical. The composition of 'deweylite' is variable; its $MgO:SiO_2$ ratio lies between those of talc and serpentine and it can contain up to 5 % NiO. Kato (1961) used DTA, infra-red spectroscopy, electron microscopy, and chemical analysis to examine several minerals of this group. He concluded that nickel-gymnite, genthite, garnierite, and deweylite were all mixtures of 1:1 and 2:1

layer silicates, that is serpentine and talc or their nickeliferous counterparts. A detailed study of a natural 'deweylite' from Pennsylvania, by Lapham (1961) showed that it was a poorly crystallized magnesium silicate hydrate containing nickel, which was of low-temperature origin and had been formed in colloidal suspension. He described it as a member of the serpentine group deficient in octahedral ions: a kind of dioctahedral antigorite. Faust and Fahey (1962) used all of the methods employed by Kato in their extensive examination of minerals in the MgO–SiO_2–H_2O system. As a result of this work they showed that deweylite was a mixture of serpentine and stevensite (the magnesium end-member of the montmorillonite series). The close similarities that exist between the badly crystallized magnesium silicate hydrates and the nickel magnesium silicate hydrates were pointed out by Faust (1966), who asserted that garnierite, nickel-gymnite, genthite, deweylite, and several other minerals were all mixtures of nickeloan serpentine and pimelite.

Conclusions reached by these workers regarding the composition of 'deweylite' apply only to those specimens included in the various studies and not necessarily to the original or type materials, which were not examined during any of the reported investigations.

Synthesis. Attempts were made to synthesize deweylite by the hydrothermal treatment of magnesia-silica gels of various compositions, over a range of pressure and temperature conditions. It is reported that the $MgO:SiO_2$ mole ratios of the natural mineral can be as low as 0·9 and reach almost as high as those of the serpentines ($\sim$ 1·5).

Three starting materials compositions were chosen, having Mg/Si ratios of 0·8, 1·0, and 1·2; in addition, two further Mg/Si 1·0 gels containing 3 and 6 % NiO were prepared. They were made by adding colloidal silica sol (Syton 2X) to a stirred aqueous solution of AR magnesium nitrate and, where necessary, AR nickel nitrate, and evaporating the resulting mixture to dryness. The dry powder was then ignited at 650–700 °C in a platinum dish until all nitrate had been removed.

Most of the experiments were carried out at low (saturated steam) pressures in hydrothermal bombs of the type described by Barrer (1948), although several high-pressure runs were also made. In the latter case, the starting materials were sealed in gold capsules with added water and subjected to the desired conditions in a Tuttle cold-seal apparatus (Tuttle, 1949).

X-ray analysis. The phases present in the resulting materials were identified by X-ray diffraction methods and the results obtained are presented in table I. Detailed X-ray powder spacings for three of the synthetic preparations are compared with literature data for 'deweylite', clinochrysotile, and talc in table II.

The term 'disordered intermediate' used in table I refers to a very poorly crystallized material that gave an X-ray powder pattern consisting of only four or five broad bands (see Specimen 6D, table II). These are the same bands that Majumdar and Rehsi found in the X-ray patterns of their autoclaved mixtures of high-magnesia cement and fly-ash. The material giving this pattern was generally formed at low

temperatures and pressures after short reaction times but was never encountered when nickel-containing starting materials were used. It was apparently an intermediate in the formation of both talc-like and serpentine-like materials since these were the only reaction products identified in runs carried out at higher temperatures and pressures and after longer times. The badly crystallized talc and serpentine (e.g. Specimens 27D and 20D respectively, table II) gave similar X-ray patterns, which consisted of the four or five broad bands mentioned above plus diffuse lines centred on either 10 Å and 3·15 Å (talc) or 7·3 Å and 3·65 Å (serpentine).

TABLE I. *Conditions of preparation of magnesium silicate hydrates*

No.	$\dfrac{MgO}{SiO_2}$	T	MN/m^2	Days	Product	No.	$\dfrac{MgO}{SiO_2}$	T	MN/m^2	Days	Product
8D	0·8	180 °C	1·00	28	D	24D	1·2	255 °C	4·22	21	D
6D	1·0	180	1·00	28	D	21D	0·8	282	6·55	13	T
17D	1·0*	180	1·00	90	S	35D	1·0	290	214·40	35	T
18D	1·0†	180	1·00	90	S	27D	1·0	290	7·34	30	T
11D	1·2	180	1·00	88	D	19D	1·0*	282	6·55	7	S
32D	1·0	216	219·30	50	T	16D	1·0†	293	7·67	7	S
1D	1·0	238	3·14	30	T	25D	1·0†	282	6·55	30	S
34D	1·0	244	93·80	35	T	13D	1·2	282	6·55	13	S
30D	1·2	250	171·70	14	S	31D	1·5	307	214·40	54	S
33D	1·0	252	186·90	44	T	14D	1·0	315	10·50	7	T
23D	0·8	255	4·22	13	T	26D	1·0	350	16·4	30	T
2D	1·0	258	4·43	5	D	40D	1·5	383	251·00	34	S_x
15D	1·0*	255	4·22	7	S	36D	1·0	390	179·30	21	T
20D	1·0†	258	4·43	7	S	37D	1·0	503	220·60	28	T_x

* Plus 3 % NiO.
† Plus 6 % NiO.
Phases detected by X-rays: D, disordered intermediate; S, badly crystallized serpentine; T, badly crystallized talc; S_x, serpentine; T_x, talc.

Microscopy. Most of the synthetic magnesium silicate hydrate preparations were examined optically and their mean refractive indices measured. The materials were in all cases fine grained and contained no fibrous component; because of this no other optical constants could be measured. They showed low birefringence and their mean refractive indices were all in the range 1·534–1·560, the specimens with higher Mg/Si ratios and those containing nickel tending to give the higher values. These figures compare with values of 1·504–1·555 quoted by Lapham (1961) for a large number of 'deweylite' specimens.

Two specimens of natural 'deweylite' from Cedar Hill Mine, Lancaster County, Pennsylvania were examined in thin section. Both sections showed essentially the same features with large fibrous or lamellar inclusions much in evidence in a fine grained matrix. The same two specimens were examined by scanning electron microscopy along with several of the synthetic preparations. Figs. 1 and 2 are micrographs of a green-white and a red-brown variety of the mineral; they both show a distinctly

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platy or sheet-like structure with no evidence of fibres. Fig. 3 shows the microstructure of a hydrothermally prepared magnesium silicate hydrate, which, on the basis of X-ray data, has been termed 'disordered intermediate'. The particles have no definite

TABLE II. *X-ray data. Patterns of all three synthetic preparations showed a strong diffuse line centred at about* 4·55 Å *within the* 5·8–4·2 Å *band*

Natural 'deweylite' Lapham (1961)		Specimen 6D		Specimen 20D		Specimen 27D		Clinochrysotile Whittaker and Zussman (1956)		Talc Stemple and Brindley (1960)	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
						11 ⎫ 9·5 ⎭	w			9·34	100
7·46	55			7·3	m			7·36	100		
4·552	100	5·8 ⎫ 4·55 ⎬ 4·2 ⎭	ms	5·8 ⎫ 4·55 ⎬ 4·2 ⎭	m	5·8 ⎫ 4·55 ⎬ 4·2 ⎭	m	4·58	50	4·66	90
										4·55	30
3·666	40			3·65	w			3·66	100		
										3·51	4
										3·43	1
						3·2 ⎫ 3·1 ⎭	vw/d			3·116	100
										2·892	1
		2·65 ⎫		2·65 ⎫		2·63 ⎫		2·66	40	2·629	12
2·597	35	⎪		⎪		⎪		2·594	40	2·595	30
2·500	65B	⎬	w	⎬	m	⎬	w	2·549	50		
2·450	50B	⎪		⎪		⎪		2·456	80	2·476	65
		2·40 ⎭		2·40 ⎭		2·43 ⎭					
										2·335	16
								2·282	30		
								2·215	30	2·212	20
										2·196	10
										2·122	8
								2·096	50	2·103	20
										1·930	6B
										1·870	40
								1·829	30		
		1·72	vw/d	1·73 ⎫ 1·71 ⎭	vw	1·73	vw/d	1·748	50	1·725	—
										1·682	20B
1·533	85	1·55 ⎫ 1·52 ⎭	mw	1·535 ⎫ 1·515 ⎭	m	1·53	ms	1·536	80	1·557	20
										1·527	40
										1·509	10
								1·465	30	1·460	8B
										1·406	16
										1·394	20
										1·336	16
1·320	20	1·32 ⎫ 1·30 ⎭	vw	1·32 ⎫ 1·30 ⎭	vw	1·325 ⎫ 1·31 ⎭	w	1·317	40	1·318	10

morphological features but a complete absence of fibrous material was noted. The effect of nickel substitution on the nature of the hydrothermal preparations can be seen in fig. 4. This specimen was prepared at 293 °C from a gel containing 6 % of NiO. The structure appears to be made up of masses of convoluted plates, which give the impression of a cellular formation.
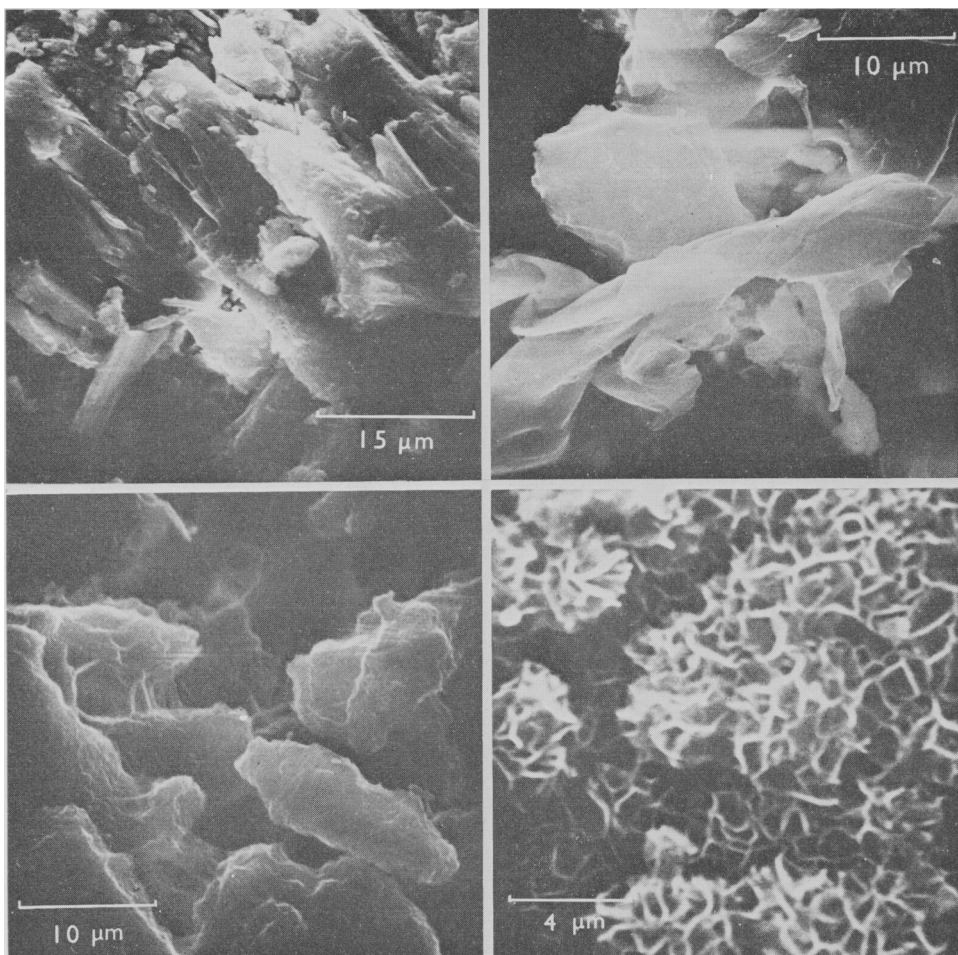
FIGS. 1–4: Fig. 1 (top left). Green-white deweylite from Cedar Hill quarry, Lancaster County, Pennsylvania. Fig. 2 (top right). Red-brown deweylite from Cedar Hill quarry, Lancaster County, Pennsylvania. Fig. 3 (bottom left). Synthetic specimen 7D. Fig. 4 (bottom right). Synthetic specimen 16D (containing 6 % NiO).

Infra-red spectra. The infra-red spectra of several natural minerals and two typical synthetic preparations are shown in fig. 5.

Comparison with standard spectra indicated that specimen 26D, which was synthesized at a relatively high temperature (350 °C), was talc. The additional band near 11·4 μm occurs quite commonly in imperfectly crystallized synthetic talcs. The spectra of a natural genthite from Texas, Pennsylvania, and the two specimens of 'deweylite' referred to earlier were virtually indistinguishable and all three appeared to resemble chrysotile rather than talc. The rather strong broad absorption centred near 16–17 μm and the suggestion of an −OH stretching vibration in the 2·74–2·75 μm region are
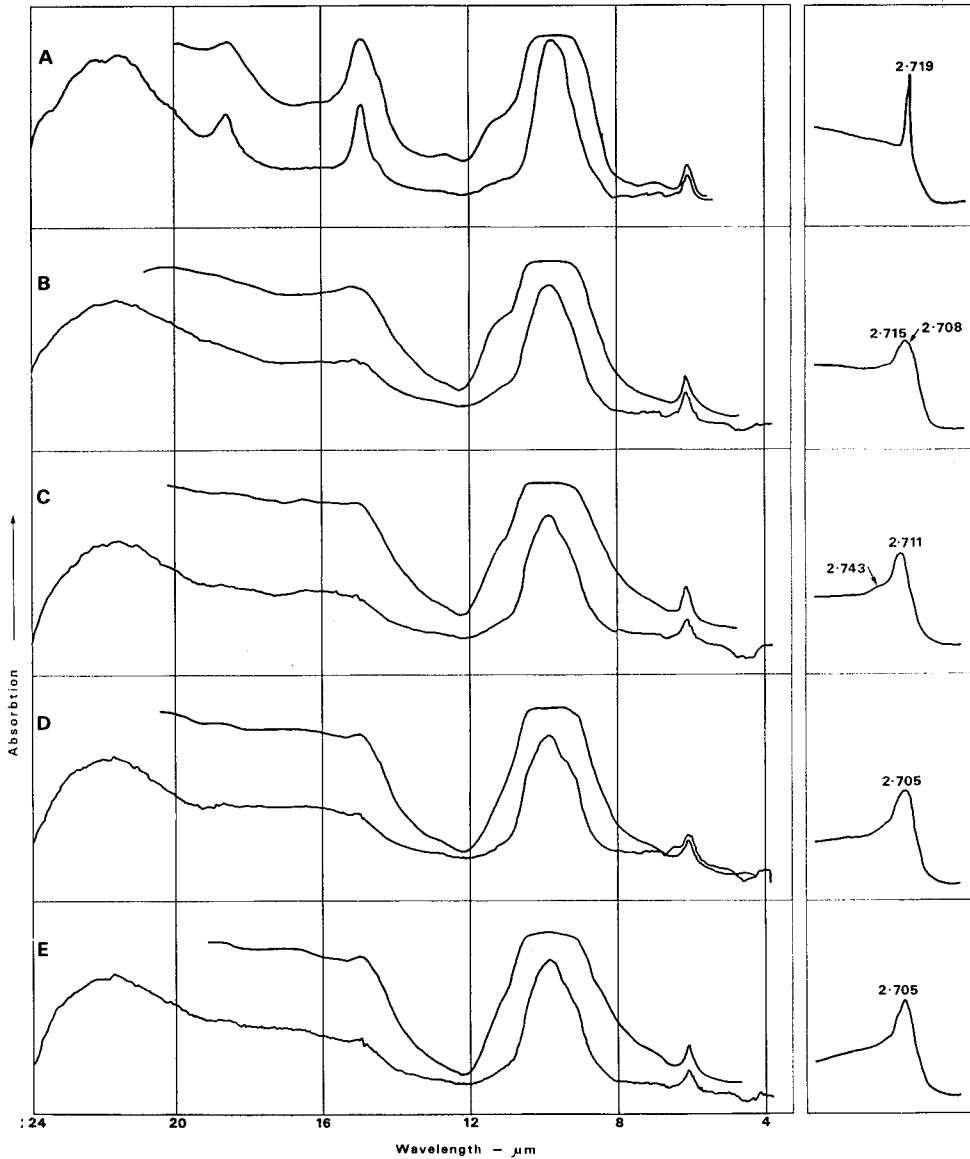
FIG. 5. Infra-red spectra: A, synthetic specimen 26D; B, synthetic specimen 20D; C, natural genthite; D, green-white deweylite; E, red-brown deweylite.

both typical of chrysotile. The synthetic nickel-containing preparation, specimen 20D, gave a spectrum very similar to those of the 'deweylites' and genthite. However, both the natural 'deweylite' minerals examined and the synthetic nickeliferous material showed a band near 15 μm, which typifies talc and is an —OH rocking frequency.

There was no evidence to show that any of the specimens examined contained free silica or brucite, but the band at about 6·1 μm in the spectra showed that they contained substantial amounts of adsorbed water. The crystalline minerals talc and chrysotile, however, show little absorption in this region.

Differential thermal analysis. The two synthetic preparations used in the infra-red study were also examined by DTA along with the two specimens of 'deweylite'. The curves, which were recorded on a Stanton 'Standata' instrument operating with a heating rate of approximately 10 °C per minute, are presented in fig. 6.

The natural 'deweylites' (curves 2 and 4) gave almost identical traces, which showed low-temperature endotherms in the 50–80 °C region followed by further endothermal effects at 600–50 °C. These almost certainly represent the loss of adsorbed and constitutional water respectively. Both specimens also showed two exotherms between 800 and 830 °C, which, according to Lapham, indicate the crystallization first of forsterite then of enstatite. Curve 3 for specimen 20D, which is a nickel containing material, is essentially the same as those of the mineral up to the recrystallization region; here only one peak appeared and it occurred at the same temperature as the higher of the two 'deweylite' exotherms. A Rhodesian chrysotile from Shabani was also examined for comparison purposes (curve 6); the thermogram was broadly similar to all three mentioned in the foregoing descriptions except for the presence of two small exotherms at 270 and 300 °C, and the position of the dehydroxylation endotherm at 709 °C. Low-temperature exotherms between 250 and 400 °C in serpentines have been noted by several workers (Kourimsky and Satava, 1954; Faust and Fahey, 1962) but their origins have not yet been explained. The single exotherm at 822 °C is in the same position as that of the synthetic nickel-bearing specimen. X-ray examination of specimens of all these four materials after heating to 1100 °C showed the presence of enstatite and forsterite only. The 'deweylites' and specimen 20D gave predominantly enstatite with minor amounts of forsterite while chrysotile formed forsterite as the major product.

The remaining two curves, those of specimen 26D (curve 1) and natural talc (curve 5), show little detail but have obvious similarities. The shallow endothermal dehydration effects occur at about 820–80 °C in the synthetic material against 880–980 °C in talc. These temperature differences, like that noted earlier between the dehydration peaks of chrysotile and specimen 20D, can be readily explained in terms of the crystallinity of the materials. Well-crystallized minerals such as talc and chrysotile would be expected to lose structural hydroxyl groups at a higher temperature than their synthetic, less-ordered counterparts.

Discussion. The results of the present examination of specimens of natural 'deweylite' from a locality in Pennsylvania indicate that the mineral is not a single compound but a mixture of two disordered materials. The infra-red spectral evidence shows that it exhibits many of the characteristics of chrysotile, but the presence of an absorption band near 15 μm gives a strong indication that it also contains talc as a second component. Differential thermal analysis evidence also points to the presence of serpentine
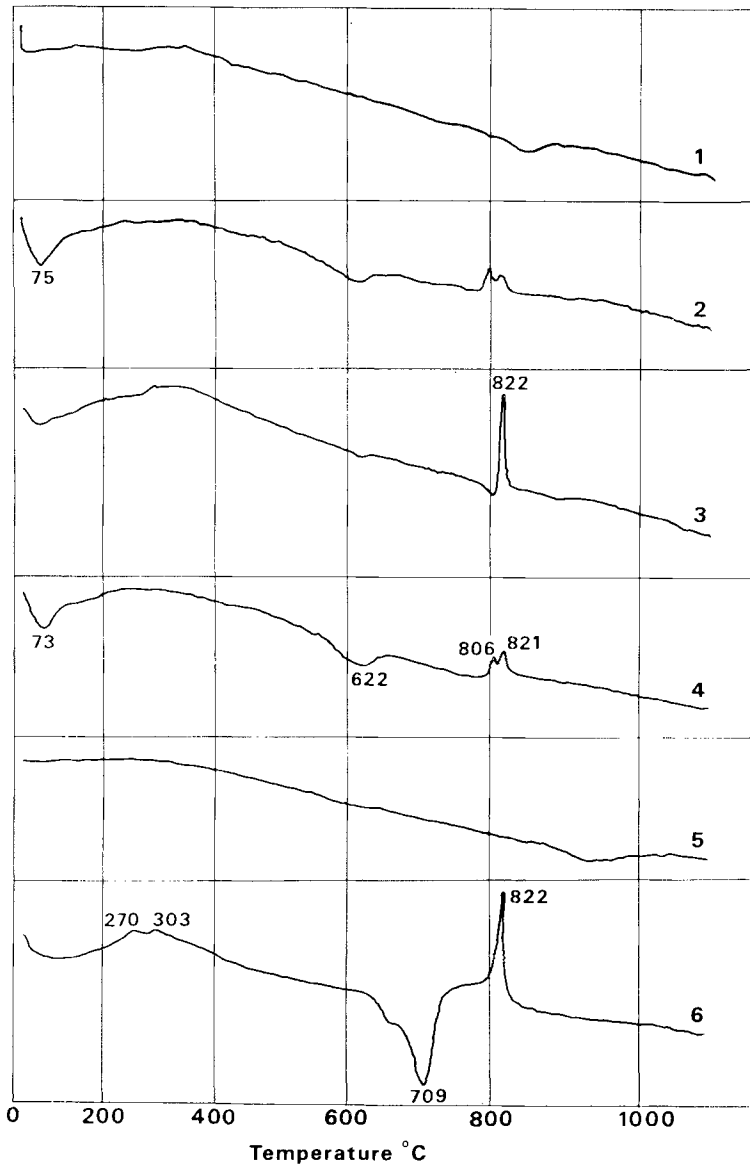
FIG. 6. Differential thermal analysis curves: 1, synthetic specimen 26D; 2, red-brown deweylite; 3, synthetic specimen 20D; 4, green-white deweylite; 5, talc; 6, chrysotile.

in the minerals but because of the indefinite nature of the talc curve its presence could not be confirmed. The X-ray data are less easily interpreted because of the dependence of this technique on long-range order, which the 'deweylites' do not show. The two most characteristic long spacings of serpentine, 7·3 Å and 3·65 Å, both appear in the 'deweylite' patterns and a smudge in the region of 10 Å, which Lapham attributed to sepiolite impurity, indicates that talc might also be present, particularly in view of the other evidence. The remainder of the patterns are too indefinite to assign bands to either one or other of these proposed components.

The nature of the materials made from magnesia-silica gels depended on the conditions of synthesis and on the original gel composition. At 180 °C the disordered intermediate was formed from all compositions except those containing nickel. Treatment at higher temperatures resulted in the development of a talc-like structure in the Mg/Si 0·8 and 1·0 compositions while the Mg/Si 1·2 and the nickel-containing materials formed products having elements of a serpentine structure. Higher pressures caused the differentiation of the intermediate to take place at lower temperatures. At the highest temperatures used, well crystallized talc and serpentine were formed. The formation of 'talc' from the starting materials with Mg/Si of 0·8 and 1·0, and 'serpentine' from those with an Mg/Si of 1·2 is understandable on equilibrium grounds, since these compositions would give mixtures containing approximately 90, 58, and 31 % talc respectively; in all cases only the major equilibrium phase was detected.

It may now be suggested that the synthetic materials, hitherto referred to as 'disordered intermediate' and 'badly crystallized serpentine' are in fact identical to natural 'deweylite' or nearly so. The differences apparent in the experimental data are slight and are thought to result from differences in their physical structures rather than in their chemical or mineralogical compositions. Specimen 20D was shown to give an infra-red spectrum the same as that of 'deweylite' whereas there were some small differences in detail between their respective X-ray patterns and DTA traces. The two last-mentioned sets of results are influenced by long-range order while infra-red spectroscopy measures structural features that are localized. 'Deweylite', therefore, appears to be a relatively coarse mixture of poorly crystallized talc and poorly crystallized serpentine. The X-ray pattern shows the basal spacings of both components and during differential thermal analysis the separate domains crystallize independently to forsterite on the one hand and enstatite on the other, producing two distinct peaks. The synthetic preparations, however, are intimately interlayered, do not show distinct basal spacings, and forsterite and enstatite crystallize simultaneously during heating. The appearance of a weak 7·3 Å spacing in the poorly crystallized serpentine material indicates that the serpentine component has a slightly higher degree of crystallinity than the talc with which it is mixed.

'Deweylite' is obviously of low-temperature origin, possibly formed well below 180 °C, and is apparently metastable with respect to talc and serpentine. However, the slowness of the crystallization process at low temperatures would explain its occurrence as a mineral. Nickel is not an essential constituent, but it greatly assists the development of the talc-like and serpentine-like phases from the intermediate material.

It seems possible that this type of product might develop in room-temperature-cured hydrated high-magnesia cements after long periods, as an indistinct gel-like material showing the same four or five X-ray bands as the hydrothermal products.

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